



The performance degradation of a passive direct formic acid fuel cell and its improvement by a hydrophobic filter

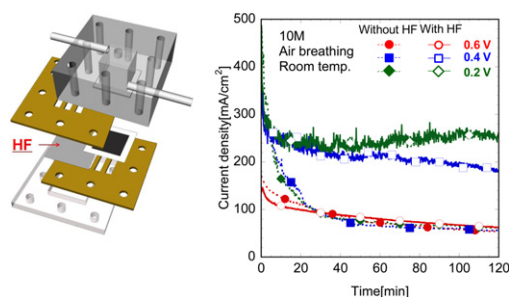
Takuya Tsujiguchi*, Soshi Hirano, Takanori Iwakami, Nobuyoshi Nakagawa

Department of Chemical and Environmental Engineering, Gunma University, 1-5-1 Tenjin, Kiryu, Gunma 376 8515, Japan

HIGHLIGHTS

- The effect of the flooding on the power generation characteristics of the DFAFC was investigated.
- The cathode over-potential significantly increased due to the flooding.
- To inhibit the flooding, a hydrophobic filter was inserted to the cathode surface.
- The cathode over-potential significantly decreased by inserting hydrophobic filter.

GRAPHICAL ABSTRACT



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ABSTRACT

A direct formic acid fuel cell, DFAFC, can generate a higher power density compared with other direct liquid fuel cells, however, its performance decreases with time. Especially in a passive operation, the performance degradation was caused not only by catalyst poisoning at the anode but also serious flooding at the cathode due to high current operation. In this study, the effect of the flooding on the power generation characteristics of the DFAFC operated with three different air supplying modes, i.e., air breathing, air flowing and oxygen flowing, was investigated by comparing the cathode over-potential before and after 2 h operation at a constant voltage. Moreover, in order to inhibit the flooding, a hydrophobic filter, HF, was introduced at the surface of the cathode, and the effect of the HF on the flooding was investigated. It was found that the water crossover from the anode to the cathode significantly increased by the electroosmotic effect at a high current density, and it caused serious flooding when DFAFC was operated without HF. On the other hand, by inserting the HF, the performance degradation could be inhibited by reducing the flooding at the cathode surface, and the cathode over potentials could be improved. The HF is necessary for higher power generation and a stable operation of the passive DFAFC.

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1. Introduction

There has been considerable interest in the use of a direct liquid fuel cell as an alternative battery for portable electric devices. Especially, direct formic acid fuel cells, DFAFCs, have been considered as a candidate for portable power sources due to the high power density using a Pd catalyst for the anode [1–3], limited fuel

crossover [4–6], a high theoretical open circuit voltage [1]. The high power density of the DFAFC, which was 6 times higher than that of the direct methanol fuel cell (DMFC) [2], and equivalent to that of a polymer electrolyte hydrogen fuel cell (PEFC), is quite attractive even though the theoretical energy density of the DFAFC is lower than that of the DMFC. Furthermore, DFAFC can be operated with a passive mode without using any external pumps for the fuel supply. Therefore, the passive DFAFC has been expected to generate high power with a compact system, and it has been intensively developed nowadays [3,7–16].

* Corresponding author. Tel.: +81 277 30 1459; fax: +81 277 30 1457.

E-mail address: tsujiguchi@cee.gunma-u.ac.jp (T. Tsujiguchi).

Although the DFAFC with Pd for an anode catalyst showed an excellent performance, the performance decreased with time. It has been known that performance degradation is caused by a poisoning of the Pd at the anode [17–20]. Hence, alternative materials, such as PdPb/C [19], and Pd–V [20], have been investigated as resistive catalysts to the poisoning by enhancing the oxidation of intermediates via bi-functional mechanism, although the species of the poisoning is still unclear. These studies were conducted with three electrode cells or an active operation. So far, there have been few studies about the performance degradation with time occurring in a passive DFAFC. Passive DFAFC is likely to be affected by the flooding since it generates a high current density. Ha et al. reported that the performance of the passive DFAFC is limited mainly by the poor mass transport of the cathode [3] by measuring the distinct anode and cathode potentials during the acquisition of the cell polarization, although they did not mention the effect of the flooding. Although the mass transport limitation at the cathode was pointed out in elsewhere [14–16], the effect of the flooding on the power generation characteristics of DFAFC has not been experimentally investigated. Therefore, it is important to investigate the effect of the flooding on the power generation characteristics and the way to inhibit the flooding to achieve a stable power generation.

In this study, the effect of the flooding on the power generation characteristics was investigated under three air-supplying modes, air breathing, air flowing and oxygen flowing, by comparing the increase of the cathode over-potential for 2 h. Moreover, in order to improve the power generation, the effect of the introduction of a hydrophobic filter, HF, on the cathode was investigated under the three air-supplying modes. Water crossover and formic acid crossover during the constant voltage operation were also measured to discuss the mass transport in the DFAFC.

2. Experimental

2.1. Membrane electrode assembly (MEA) preparation

Nafion 117 (Dupont) was used as the polymer electrolyte membrane. In order to activate the proton conductivity, the membrane was pretreated by sequential immersion in boiling solutions of 3 vol.% H_2O_2 , de-ionized water, 0.5 mol l^{-1} H_2SO_4 , and de-ionized water, in that order for 1 h. Palladium black (Alfa Aesar.) and platinum black (HiSPEC 1000, Johnson Matthey Fuel Cells Co., Ltd.) were used as catalysts for the anode and the cathode, respectively. The catalyst inks were prepared by dispersing an appropriate amount of the catalyst in a solution of de-ionized water, isopropyl alcohol, and 5 wt.% Nafion solution (Wako Pure Chemical Industries, Ltd.). For the anode, the Pd ink was coated on the micro porous layer, which was prepared with 1 mg cm^{-2} of a carbon black containing 10 wt.% Nafion on the carbon cloth (35% Teflonized, ElectroChem, Inc.), to form the electrode. For the cathode, the Pt ink was coated on the carbon paper (35% Teflonized, ElectroChem, Inc.) with the micro porous layer in a similar manner. The catalyst loadings were 8 mg cm^{-2} for Pd, the anode, and Pt, the cathode, respectively. The ionomer loadings of the catalyst layer were 15 wt.% for the anode and 10 wt.% for the cathode. The MEA was then fabricated by sandwiching the membrane between the anode and the cathode and hot pressing them at 408 K and 5 MPa for 3 min. The projected area of the electrode was 4.84 cm^2 (2.20×2.20 cm).

2.2. Cell structure and hydrophobic filter

Fig. 1 shows a schematic diagram of the cell with the reference electrode, (a), and the components of the cell, (b). A fuel reservoir,

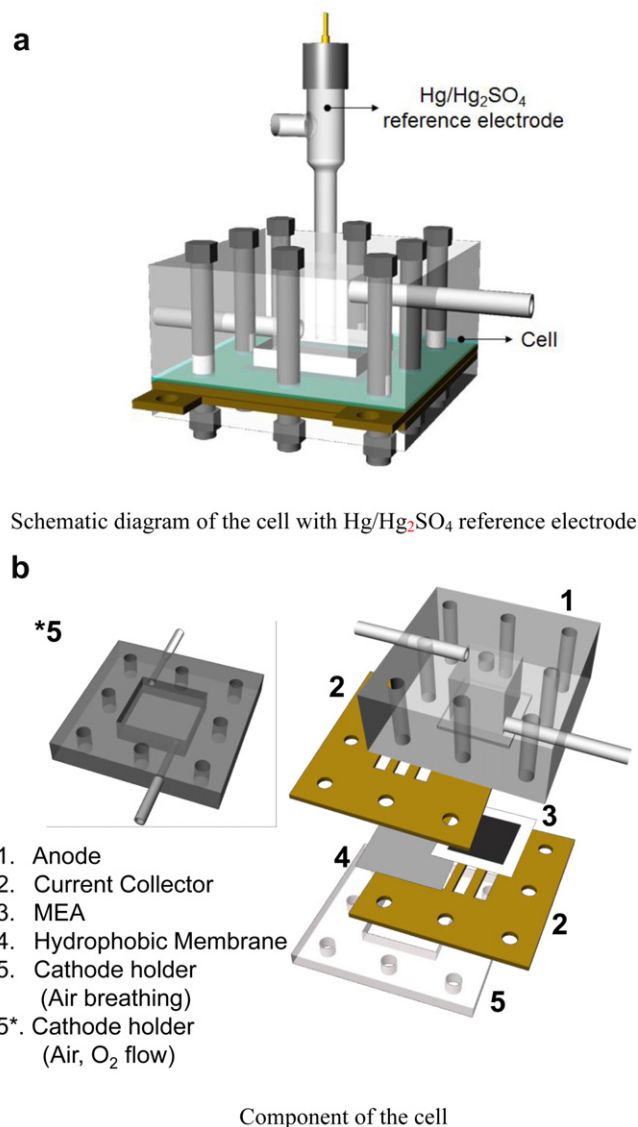


Fig. 1. Schematic diagrams of the experimental set up.

12 cm^3 in capacity, was prepared in the anode compartment. There is a small hole at the top of the fuel reservoir to insert the reference electrode. The MEA was sandwiched between the two current collectors, which were plates of stainless steel, 1 mm, coated by gold with open holes, and 74% open ratio. In a semi-passive operation with flowing air or oxygen, cover 5* which separates the cathode from surrounding air was used by replacing cover 5.

In some operations, the hydrophobic filter, HF, 4, was inserted between the cathode and the cathode current collector. HF was prepared by coating a carbon black layer, 1 mg cm^{-2} carbon black on the carbon paper with FEP, fluorinated ethylene propylene copolymer, solution and heating it to 100 °C for 1 h. The FEP solution was prepared by diluting the FEP dispersion (FEP 120-JR, Du-Pont-Mitsui Fluorochemicals CO., Ltd.) with water. The concentration of the FEP solution was 12 wt.%. The FEP coating was repeated several times until the FEP content reached 0.5 mg cm^{-2} . The contact angle to water of hydrophobic filter was measured by contact angle meter (CA-D, Kyowa Interface Science CO., LTD.). The contact angle to the water was 138.6°. The projected area of the filter was 4.84 cm^2 which was same as that of the electrodes.

2.3. Measurement of the power generation characteristics

The DFAFC was operated under three air supplying modes, air breathing, air flowing and oxygen flowing, in order to investigate the influence of the mass transport at the cathode in the cases both with HF and without HF. In the air breathing operation, air was passively supplied to the cathode via openings of the cathode holder. On the other hand, in the air flowing and the oxygen flowing operation, 200 ml min⁻¹ of air or oxygen was supplied to the cell. All experiments were conducted in the room condition, 1atm, 293–298 K. A formic acid solution was prepared by diluting formic acid (special grade reagent, Wako Pure Chemical Industries, Ltd.) with distilled water (Kyoei Pharmaceutical Co., Ltd.). The current–voltage, *i*–*V*, characteristics of the DFAFC were measured by linearly sweeping the voltage from the open circuit voltage to zero at the scan rate of 2 mV s⁻¹. The electrode potentials versus the Hg/Hg₂SO₄ reference electrode (BAS Inc.) were recorded to the data logger (GL 200, Graphtech) during the *i*–*V* measurement. All the potentials in this paper were referred to normal hydrogen electrode (NHE). The over-potentials were determined by the subtracting the potential at certain current from the potential at the open circuit potential, i.e., the potential at 0 mA cm⁻². The current versus time, *i*–*t*, characteristics were measured at different cell voltages, 0.2 V, 0.4 V and 0.6 V. The *i*–*t* and *i*–*V* measurements were conducted using an electrochemical measurement system (Hz-5000, Hokuto Denko, Co., Ltd.). The entire cell weight and the concentration of the solution were also measured at the beginning and the end of the *i*–*t* measurement to calculate the formic acid and water crossovers. The formic acid concentration was measured by gas chromatography equipped with a TCD detector and a Porapak T column (Shimadzu, GC14-B).

Since the anode performance degraded with the operation due to the catalyst poisonings, the following regeneration process, RP, was conducted. After power generation, the formic acid solution was replaced with fresh water and the cell was swung to wash the anode surface. This washing was repeated until the residual cell voltage decrease to 0.1 V under according to the previous report by Zhou et al. [21]. The anode performance was completely regenerated by this RP process. The degradation due to the flooding during the *i*–*t* measurement was evaluated as follows. First, the *i*–*V* measurement recording the anode and the cathode potentials was conducted for the performance “before *i*–*t* measurement”, and then the RP was conducted. After RP, the *i*–*t* measurement was carried out at different cell voltages. Next, the *i*–*V* measurement was repeated after replacing the fuel with a fresh one for the performance “after *i*–*t* measurement”. Finally, the RP was conducted to regenerate the performance to the initial one.

2.4. Calculation of the formic acid and water fluxes

The average flux for each formic acid and water across the MEA during the *i*–*t* measurement was calculated on the basis of weight loss and a decrease in the formic acid concentration of the solution. The weight loss, ΔW , which was obtained by subtracting the final weight of the remaining solution in the reservoir at the end of the *i*–*t* measurement, W_e , from that of the initial weight, W_i , can be expressed as follows:

$$\Delta W = W_i - W_e = \Delta W_{cf} + \Delta W_{cw} + \Delta W_{rf} \quad (1)$$

where ΔW_{cf} and ΔW_{cw} are the weight losses of the formic acid and that of water due to the crossover from the anode to the cathode, respectively. The ΔW_{rf} is the weight loss of the formic acid consumed by the anode reaction, calculated by integrating the area of the *i*–*t* curve assuming the complete oxidation of formic acid:

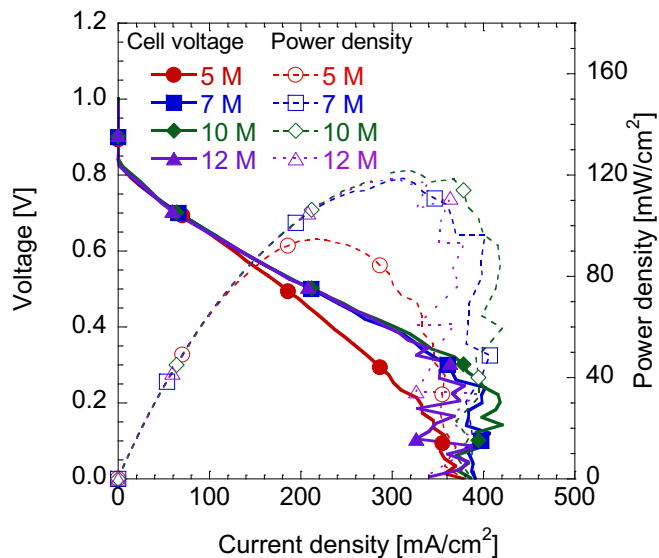


Fig. 2. Influence of the formic acid concentration on the *i*–*V* characteristics of the DFAFC with air breathing.



as follows:

$$\Delta W_{rf} = \frac{M_f A \int_0^t i(t) dt}{2F} \quad (3)$$

where M_f is the molecular weight of the formic acid, A is the apparent electrode area, t is the time of the *i*–*t* measurement and F is Faraday's constant. The ΔW_{cf} and ΔW_{cw} can be expressed as follows:

$$\Delta W_{cf} = M_f (C_i V_i - C_e V_e) - \Delta W_{rf} \quad (4)$$

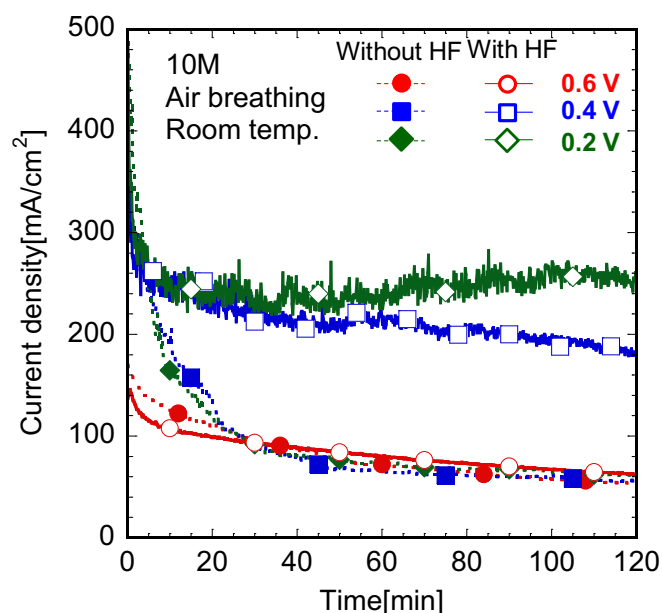


Fig. 3. Effect of HF on the current density profiles at different cell voltages with air breathing.

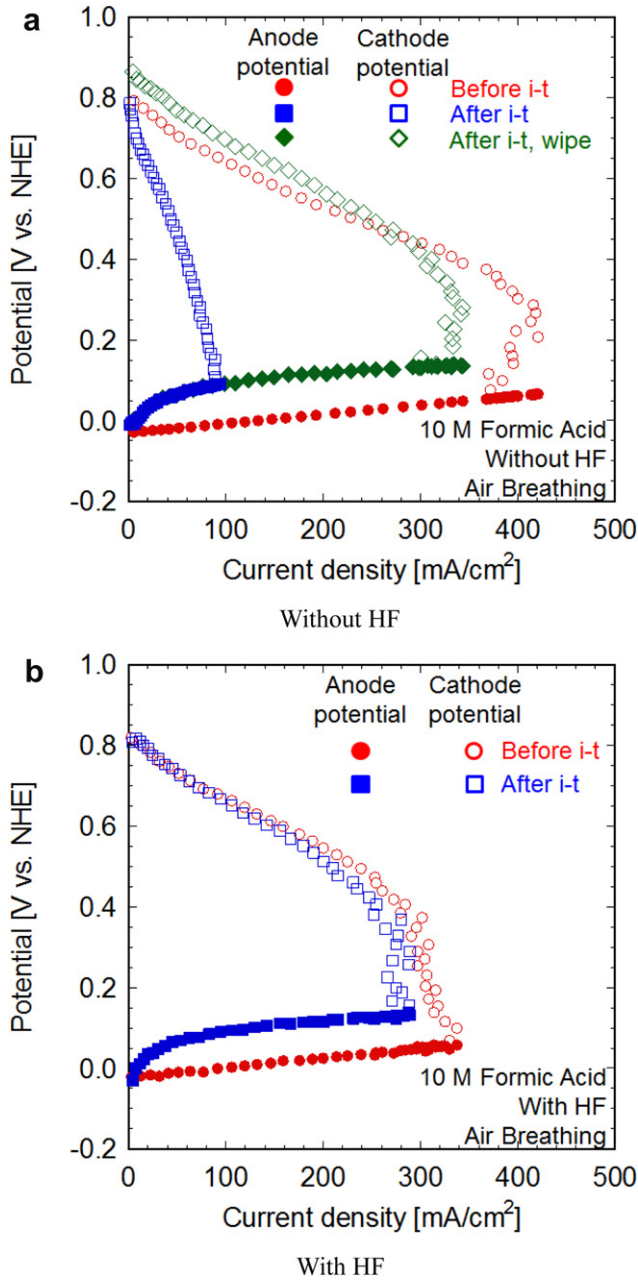


Fig. 4. Comparisons of the electrode potentials before and after i - t measurement with air breathing at 0.4 V without HF to that with HF.

$$\Delta W_{cw} = \Delta W - M_f(C_i V_i - C_e V_e) \quad (5)$$

where C_i and V_i are the formic acid concentration and the volume of the formic acid solution in the reservoir at the start of the i - t measurement, respectively, and C_e and V_e are those at the end of the i - t measurement, respectively. Hence, the crossover flux of the formic acid, J_f and that of the water, J_w , were calculated as

$$J_f = \frac{\Delta W_{cf}}{\Delta t} \quad (6)$$

$$J_w = \frac{\Delta W_{cw}}{\Delta t} \quad (7)$$

3. Result and discussion

3.1. Performance with air breathing

Fig. 2 shows the influence of the formic acid concentration on the i - V characteristics of the DFAFC operated with air breathing. The i - V characteristics were almost the same between 7 M and 12 M in accordance with the previous study [3], and the best performance was obtained at 10 M. Therefore, 10 M formic acid was used for the power generation in the following experiments. Large fluctuations of the current density appeared at a high current density, over 300 mA cm^{-2} , i.e., below 0.4 V, suggesting that a limitation of the oxygen transport due to the flooding at the cathode.

Fig. 3 shows the effect of inserting the HF on the current density profiles at different cell voltages with air breathing. The current

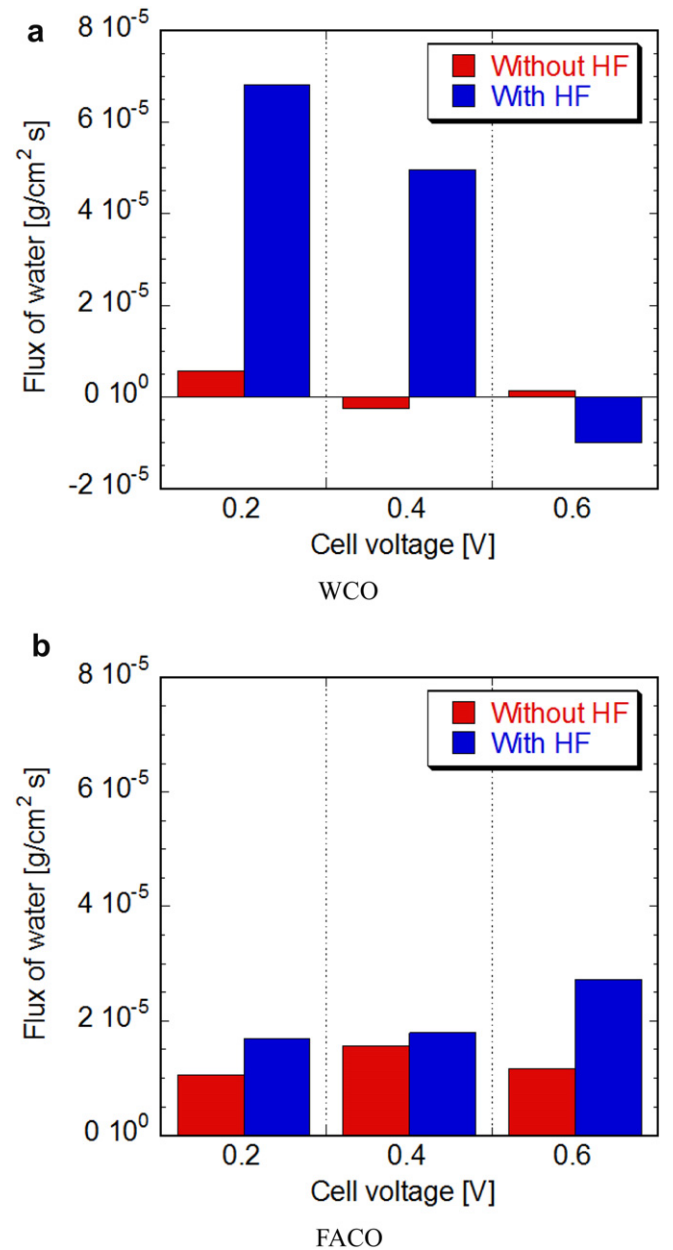


Fig. 5. Effect of HF on the water crossover, WCO, and the formic acid crossover, FACO, at different cell voltages with air breathing.

density without HF drastically decreased within 40 min when the cell voltages were 0.2 V and 0.4 V. However, in the cases using HF at 0.2 V and 0.4 V, the performance degradation could be drastically improved although sudden decreases were observed at the beginning of the operation. Moreover, serious fluctuations of the current density were observed with HF at 0.2 V and 0.4 V, suggesting that the flooding still occurred by repeating the removal of water from the cathode diffusion layer [22] although the magnitude of the flooding was reduced by the HF.

Fig. 4 shows comparisons of the electrode potentials before and after the i - t measurement at 0.4 V with air breathing without HF, in Fig. 4(a), and that with HF in Fig. 4(b). In the case without HF, the electrode potentials measured after wiping the liquid droplets at the cathode surface after the first i - t measurement were also shown in the figure. It was clear that the cathodic over-potentials were larger than the anodic over-potentials. This was due to the poor mass transport at the cathode by the air breathing operation as reported by Ha et al. [3]. Furthermore, comparing the electrode potentials before and after the i - t measurements, the cathodic over-potential significantly increased after the i - t measurement, and the performance degradation of the cathode during the i - t measurements was more remarkable than that of the anode although the anode over-potential also increased as indicated in the previous report [17–20]. On the other hand, the cathodic over-potential was improved by removing the liquid droplets from the cathode surface by wiping it, and it was recovered to that before the i - t measurement. The anode potentials were not affected by the wiping as might be expected. Therefore, it was confirmed that the degradation of the cathode was caused by flooding at the cathode surface. In a passive DFAFC, the water was easily accumulated at the cathode surface since the water removal by air flow cannot be expected. Therefore, the performance degradation due to the flooding was a serious problem in the passive DFAFC.

In contrast to this, by inserting the HF, as shown in Fig. 4(b), no change in the cathode potential between the before and after the i - t measurement was seen. This result suggested that the flooding which occurred in the i - t measurement could be inhibited by inserting the HF. However, the HF increased the mass transport

resistance showing a lower limiting current at around 250 mA cm^{-2} , compared with that without HF, about 400 mA cm^{-2} before the i - t measurement.

Fig. 5 shows the effect of the HF on the water crossover, WCO, and the formic acid crossover, FACO, during the i - t measurement are shown in Fig. 3. The positive value of the flux means the permeation through the membrane from the anode to the cathode, and the negative one means the opposite. It was noteworthy that the WCO significantly increased at cell voltages of 0.2 V and 0.4 V with HF. These were due to the operation at high current densities, i.e., electroosmotic effect, and this will be discussed in the latter section. The FACO in the case with HF was slightly higher than that without HF, and it increased when increasing the cell voltage, although the FACO without HF showed no dependency on the cell

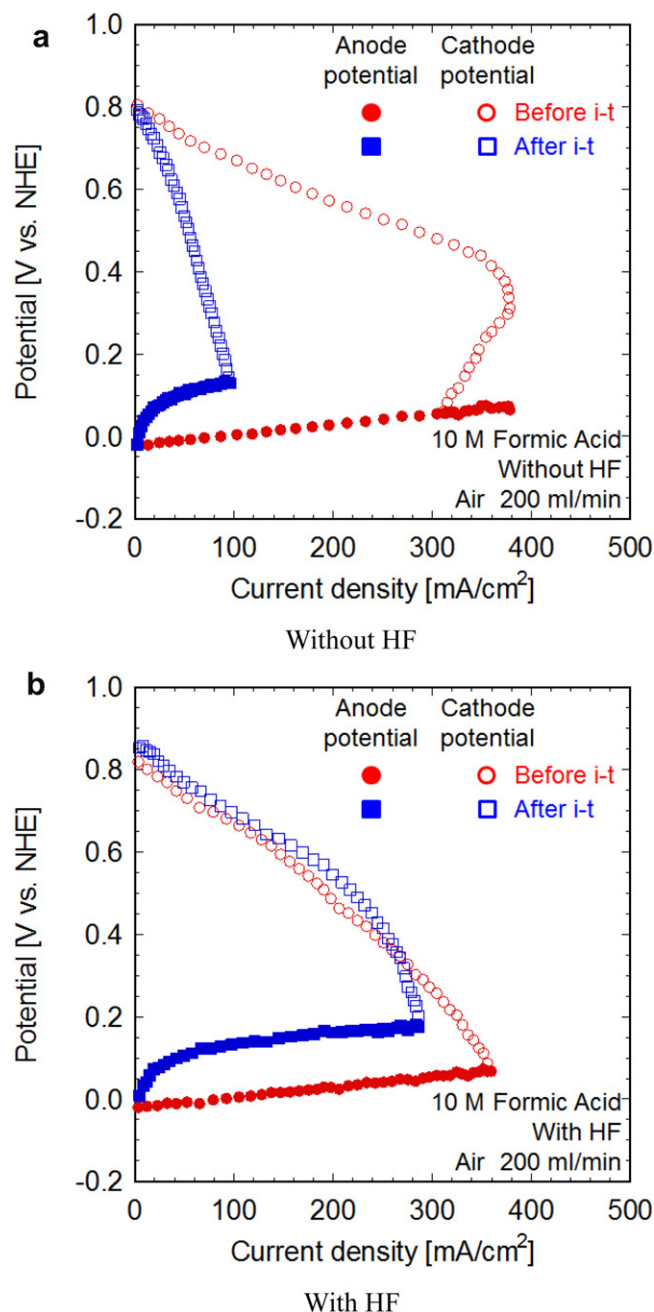


Fig. 7. Comparisons of the electrode potentials before and after i - t measurement with air flowing at 0.4 V without HF to that with HF.

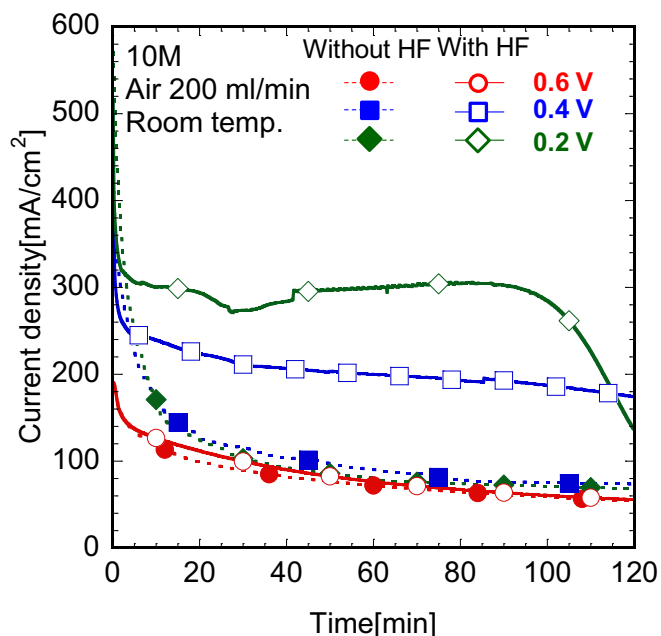


Fig. 6. Effect of HF on the current density profiles at different cell voltages with air flowing.

voltage. The reason for the increase of the FACO by inserting the HF would be due to an increase in the current density, an electroosmotic effect, similar to the WCO. The increase of the FACO when increasing the cell voltage observed in the case with HF could be due to a decrease in the formic acid consumption by the electrode reaction.

3.2. Performance with the air flowing

Fig. 6 shows the effect of HF on the current density profiles at different cell voltages with flowing air, 200 ml min^{-1} . Current densities without HF significantly decreased, and the performance degradations could be inhibited by inserting the HF at 0.2 V and 0.4 V similar to the case of air breathing as shown in Fig. 3. However, no fluctuations in the current density were observed during the operation. This was due to the mass transport improvement in the cathode diffusion layer by promoting the removal of the water in the cathode diffusion layer. The sudden decrease in the current density at 0.2 V around 100 min was caused by the depletion of the fuel due to the high current operation. Consequently, the performance degradation could be further improved by inserting the HF with the flowing air. However, the performance degradations at the beginning of the power generation were still observed. This would be caused by the limitation of the oxygen transportation, and will be discussed in the next section.

Fig. 7 shows the comparisons of the electrode potentials before and after the i - t measurement at 0.4 V with the air flowing without HF, in Fig. 7(a), and that with HF, in Fig. 7(b). In Fig. 7(a), the cathodic over-potential before the i - t measurement was slightly improved from that with the air breathing condition by improving the mass transport at the cathode, Fig. 4(a), however, the cathode potential drastically decreased after the i - t measurement even though air was supplied to the cathode during the i - t measurement. This means that the flooding at the cathode could not be removed by the air flow at 200 ml min^{-1} . On the other hand, in the case with HF, the cathode potentials before the i - t measurement remained almost the same after the i - t measurement, although the cathodic over-potential before the i - t measurement somewhat

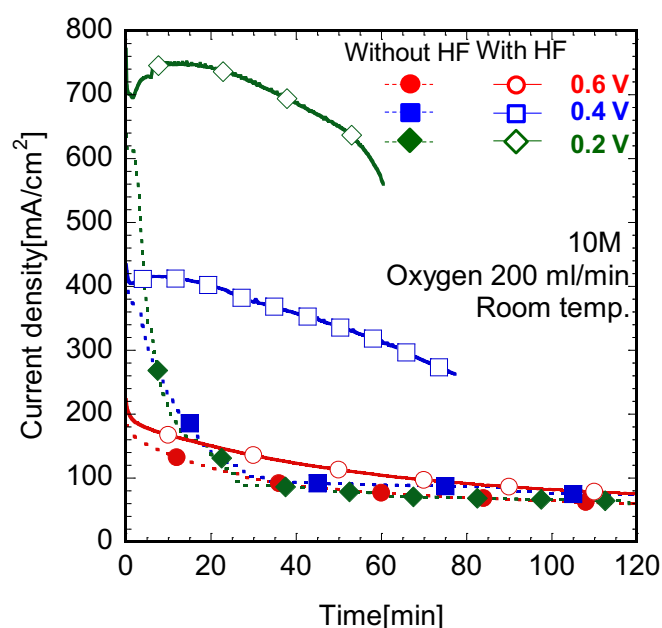


Fig. 8. Effect of HF on the current density profiles at different cell voltages with the oxygen flowing.

increased by inserting the HF. Moreover, fluctuations in the current density, observed in Fig. 4, did not appear in this case, suggesting that the flooding would be almost inhibited by inserting HF and flowing air.

3.3. Performance with the oxygen flowing

Fig. 8 shows the effect of the HF on the current density profiles of the DFAFC operated with the oxygen flowing, 200 ml min^{-1} . In the case without HF, the current densities suddenly decreased similar to the other cases operated without HF, as shown in Figs. 3 and 6, although the initial current densities were slightly higher than that of the other cases. It was suggested that the flooding inhibited the oxygen transport even when the oxygen was supplied

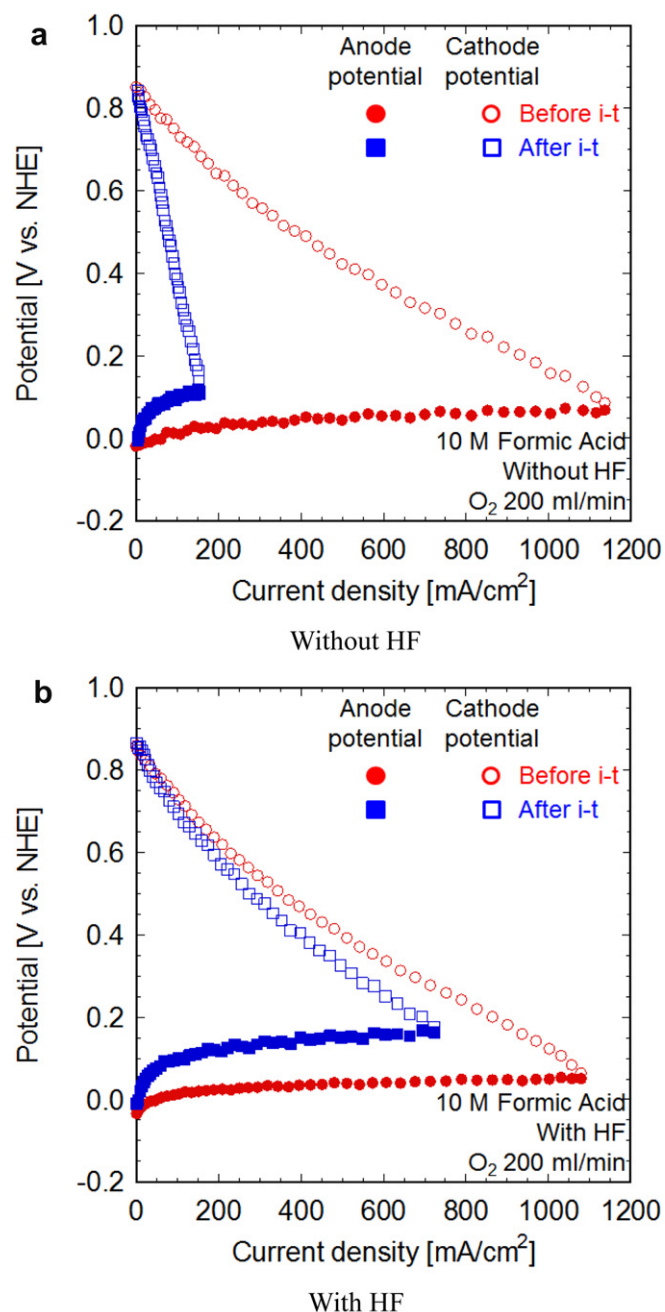


Fig. 9. Comparisons of the electrode potentials before and after i - t measurement with oxygen flowing at 0.4 V without HF to that with HF.

to the cathode, in other words, the flooding at the cathode was quite serious. In addition, it should be also noted that the cathode oxygen field in this experiment has a wide channel, so that, it was difficult for the water droplets on the cathode to be pushed out by the gas flow rate and the flooding occurred easily. On the other hand, the current densities with HF were quite higher than that without HF, and the initial performance degradations observed in the cases of the air breathing and the air flowing could be improved at 0.2 V and 0.4 V, therefore, it could be confirmed that the initial decreases in the current density were caused by the limitation of the oxygen transport.

Fig. 9 shows the comparisons of the electrode potentials before and after the i - t measurement at 0.4 V with the oxygen flowing without HF, Fig. 9(a), and that with HF, Fig. 9(b). Comparing the cathode potential before the i - t measurement without HF and with HF, it showed a similar behavior even in the high current region since the oxygen was enough to be supplied to the cathode. However, the cathode over-potential without HF significantly increased by the i - t operation. Contrary to this, by inserting the HF, the cathode over-potential slightly increased by the i - t operation since the flooding at the cathode surface could be inhibited by inserting the HF.

3.4. Water and formic acid transport characteristics in the DFAFC with HF

By inserting the HF, cathodic over-potential could be reduced and the WCO from the anode to the cathode significantly increased as shown in Fig. 4. Hence, the water transport characteristics during the i - t measurement were discussed in this section. Fig. 10 shows the influence of the average current density on the water flux during the i - t measurement shown in Figs. 3, 6 and 8. The flux of water linearly increased when increasing the average current density irrespective of using HF, suggesting that the water flux was increased by current density. In other words, water flux by the electro osmotic effect was dominant in the DFAFC. The net water-transport coefficient [23], α , was calculated as 2.20 from the slope of the line in Fig. 10. This value was similar to that of the actively operated DMFC at 30 °C and a sufficiently high current density [23] and the electro osmotic drag coefficient of Nafion 117, 1.5 to 2.6 [24].

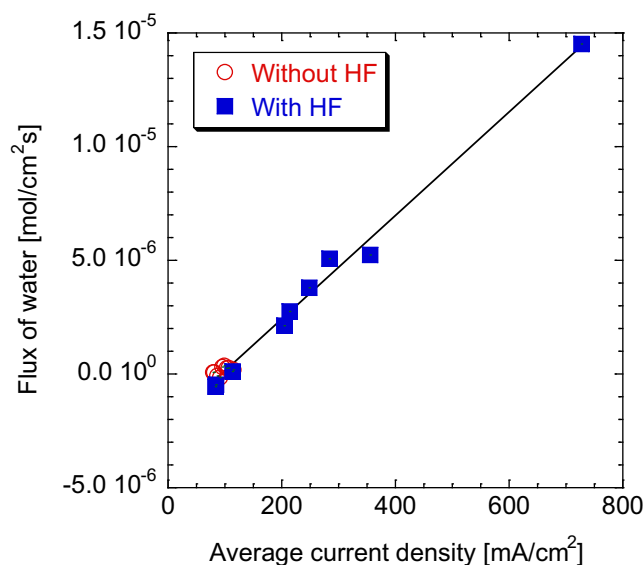


Fig. 10. Influence of the average current density on the water flux during the i - t measurement.

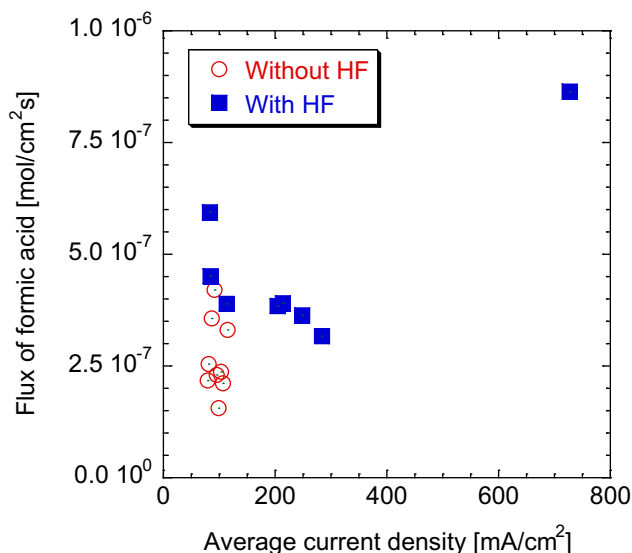


Fig. 11. Influence of the average current density on the formic acid flux during the i - t measurement.

As mentioned above, the water flux through the membrane linearly increased when increasing the current density even if the HF was inserted onto the surface of the cathode. This trend was somewhat different from the trend for a passive DMFC. A hydrophobic filter was introduced onto the cathode surface of a passive DMFC to manage the water, and the water transport characteristics of it were discussed [25–27]. In these studies, the back diffusion of the water was promoted and the evaporation of the water was reduced, hence, the total water flux from the anode to the cathode decreased when increasing the current density. Furthermore, it was also reported that the water crossover flux did not increase when increasing the hydrophobicity of the cathode backing layer and the micro porous layer [22,28]. These behaviors were caused by the increase of the liquid saturation at the cathode electrode since the liquid water cannot permeate the hydrophobic layer and/or the PTFE coated electrode. In DFAFC, the liquid water saturation would be increased by inserting the HF similar to the case of DMFC, however, the DFAFC was operated at a much higher current density than that of the DMFC, so that, the water flux linearly increased when increasing the current density.

Fig. 11 shows the influence of the average current density on the formic acid flux during the i - t measurement. The flux of the formic acid showed no dependence on the average current density. In DMFC, the methanol crossover increases when increasing the water crossover since the methanol was dissolved into the water. In contrast to this, in DFAFC, the formic acid was also dissolved into the water, however, formic acid partially dissociates in water and forms an anion (HCOO^-) which caused the repulsive interaction between the anions and the membrane sulfonic groups [1,29]. Therefore, the formic acid crossover was not increased even though the WCO was significantly increased when increasing the current density.

4. Conclusions

In this study, the effect of the flooding on the performance of the DFAFC operated with three air supplying modes, air breathing, air flowing and oxygen flowing, were investigated by comparing the cathode over voltage before and after the i - t operation. Moreover, in order to inhibit the flooding from occurring in the passive DFAFC, a hydrophobic filter, HF, was introduced at the surface of the

cathode, and the effect of the HF on the performance was investigated under three operation modes. The conclusions were indicated as follows:

- (1) Serious flooding occurred in the i – t measurement irrespective of the operation mode, and the cathode over-potential significantly increased after the i – t operation,
- (2) By inserting the HF, the performance degradation could be inhibited since the flooding at the cathode surface could be reduced irrespective of the cathode conditions. At this time, the water crossover from the anode to the cathode significantly increased in contrast to the slight increase of the formic acid crossover. The increase of the water flux also indicated the linear dependency on the current density.
- (3) Not only the flooding but also the oxygen transport resistance was a factor in the performance degradation of the DFAFC.

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